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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Elemental and organic carbon in PM_{10}: a one year measurement campaign within the European Monitoring and Evaluation Programme EMEP" *by* K. E. Yttri et al.

K. E. Yttri et al.

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General comments made by reviewer:

The paper presents a description of a background monitoring network and results from this network. Some of the work is really interesting, especially the attempts to use an OM/OC ratio based somewhat on the OC composition, the discussion of differences between PM10 and PM2.5, and source influences on the supposedly background sites.

However, I have some concerns, especially over the use (or rather, non-use) of field blank data, and non-presentation of field blank data for PM mass measurements (these are made on quartz fiber filters which tend to be brittle and could disintegrate during handling). Their method of separation of WSOC also needs clarification. There are

other points regarding their explanations for different effects seen, which are listed in "specific comments" below.

Finally, I'd like the authors to comment on the usability of these sites as "background" sites - what exactly are they the "background" for, if they are influenced by nearby polluted locations (e.g. the sites in continental Europe)? Can they really be used as background locations?

General comments to be answered:

First of all, we would like to thank the reviewer for the positive comments made to our manuscript and for the effort made to clarify and improve its content.

1.Question regarding "use (or rather non-use) of field blank data" has been merged with the specific comment concerning Page 3865, lines 7-10:

Reply: Blanks are collected and analysed to assess the amount of material (e.g. OC) found in samples, which does not come from the atmosphere, but instead from the sampling substrate itself (e.g. filters) or from contaminations (e.g. during handling or storage). We have observed that the amount of C found in filters through which particle-free denuded air has been sampled (dynamic blanks) may be twice smaller than in field blanks, which experienced exactly the same history, except that no air had been sampled through. Considering field blank levels, we would have calculated that the C concentration in particle-free denuded air was negative, which can of course not be true. The C concentration in dynamic blanks is indeed expected to be significantly positive as soon as the denuder efficiency is not 100% for VOCs that can be trapped by quartz fibre filters. This demonstrates that the amount of C found in field blanks is not suitable for determining the amount of C detected in a quartz fibre filter through which air has been sampled through, that comes from other sources but the atmosphere. This result can obviously be demonstrated sampling "zero" air only. Sampling particle-free air through a quartz fibre filter can obviously lead to enhanced C levels in these filter, when ab- and/or ad-sorbtion of atmospheric VOCs are predominant with respect

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to the volatilisation of VOC present in blank filters. This is the often-observed positive sampling artefact. However, this amount of carbon really comes from the atmosphere. It cannot be attributed to blank levels.

2.Question regarding non-presentation of field blank data for mass concentration of PM.

Reply: It is commonly known that quartz fiber filters are brittle and that this feature tends to be enhanced when the filters have been prefired. Hence, the authors fully agree with the statements made by the referee about the quality of quartz fiber filters and how this might affect the quality of the data. While we have discussed the quality of the OC data in terms of field blanks rather thoroughly (See section 3.1 and Figures 2 and 3), this has been left out for the mass concentration of PM10. The reason for neglecting this is that we wanted to focus on the carbonaceous fraction. However, the statement made by the referee is timely, as we present the PM10 data and make use of the PM10 mass concentrations when estimating the relative contribution of the carbonaceous material to PM10.

On average, the mass on the field blanks accounted for 3.6 pluss/minus 3.1% of the PM10 mass concentration on an annual basis. Thus, the uncertainty introduced by not accounting for the field blank of PM10 is only minor, indicating that we have a rather good quality of the PM10 mass concentration data, despite using quartz fiber filters. On the other hand, we recognize that this is information is important for evaluating the quality of the data and that it should have been stated in the manuscript. In order not to extend the manuscript further, we suggest to include the text mentioned below in section 3.1 to satisfy the interested reader with respect to the magnitude of the field blank levels of PM10.

"On average, the mass on the field blanks accounted for 3.6 pluss/minus 3.1% of the PM10 mass concentration on an annual basis."

3.The referee requests a "clarification of the method used for separation of WSOC".

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The water extracts was filtered using PTFE-membrane single-use syringe filters (Sartorius Minisart SRP 15). Unfortunately this was left out from the original manuscript. This part of the sample preparation has no been added to section 2.2.1. (See below).

Reply: "A total of 71 samples were subjected to WSOC (Water-soluble organic carbon) analysis. Before analysis, parts of each filter were soaked in Milli-Q water (7 ml for low volume filters and 20 ml for high volume filters) and subjected to sonication (30 min) for extraction of the WSOC. The water extracts were filtered using PTFE-membrane single-use syringe filters (Sartorius Minisart SRP 15). The dissolved organic material was then quantified using a Shimadzu TOC liquid analyzer (model TC5000A). This instrument also allows for determination of inorganic (carbonate) carbon following acidification. The inorganic carbon was subtracted from the dissolved organic carbon in order to obtain the WSOC fraction. However, the concentrations of inorganic carbon were negligible most of the time. The water-insoluble organic carbon (WINSOC) was quantified by subtracting WSOC from OC. The WSOC analysis was performed at the Institute of Atmospheric Sciences and Climate of the Italian National Research Council (ISAC-CNR)."

4.The author request that the authors comment on the usability of the sites as "background" sites - what exactly are they the "background" for, if they are influenced by nearby polluted locations (e.g. the sites in continental Europe)? Can they really be used as background locations?

Reply: The sites at which the samples were collected are established to monitor regional distribution and trends in ambient concentrations, and thus ideally not located close to any significant local emission sources. While there is long tradition to nominate such sites as background sites, it does unfortunately not mean that any local influence can be excluded. In particular the fact that such sites have been located away from key anthropogenic sources, they are often located in rural areas where you might experience more agricultural activities, or in areas where natural biological processes result in a local influence. The term "remote" is normally given for sites that

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are located even further away from anthropogenic source regions, or being located at high elevation. The major monitoring networks addressing regional and global pollution issues have harmonized their nomination of such sites (e.g. EMEP and WMO-GAW) and there is a detailed documentation of the sites and their surroundings (see e.g. www.nilu.no/projects/ccc/sitedescriptions). With respect to Air Quality monitoring networks (e.g. the monitoring is performed as prescribed by the Air Quality Framework Directive), the site criteria have been developed by the European Topic Center for Air Quality and the EIONET community. These build upon the same criteria as EMEP/GAW with respect to background and remote sites, but has in addition other classes for sites being more affected by local sources. Of relevance for this study is the classification of "urban background", which indicates that the site is not significantly affected by any specific local source(s) within the urban catchment, but rather that it provides an overall picture of the whole urban area. A further complexity is the fact that the geographical representativeness of a given observation not only depends on the compound one investigates but also on the meteorological conditions. This fact makes representativeness highly variable with time, and even sites located in urban areas can for periods be mainly influenced by emissions from a significant distance rather than on local scale. We are reluctant to put large emphasis on site representativeness in the text, and have preferred to use well-approved site classification nominations (with reference to site classifications used).

Specific comments made by the reviewer:

5.Instead of "organic molecules", suggest use "organic species".

Reply: Will use "organic species".

6.Instead of "pyrolytically generated EC", suggest use "pyrolytically generated lightabsorbing carbon" or "pyrolytically generated refractory light absorbing carbon" or better, "charred organic carbon" - the optical properties of charred organic carbon generated during the thermal-optical analysis seem to be different from that of native EC, e.g.

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Chow et al. 2004; Subramanian et al. 2006.

Reply: Will use "charred organic carbon".

7.What is an "urban background"? That seems contradictory!

Reply: With respect to Air Quality monitoring networks (e.g. the monitoring is performed as prescribed by the Air Quality Framework Directive), the site criteria have been developed by the European Topic Center for Air Quality and the EIONET community. These build upon the same criteria as EMEP/GAW with respect to background and remote sites, but has in addition other classes for sites being more affected by local sources. Of relevance for this study is the classification of "urban background", which indicates that the site is not significantly affected by any specific local source(s) within the urban catchment, but rather that it provides an overall picture of the whole urban area.

8.Section 2.2.1: WSOC analysis: Samples were sonicated for WSOC. Were the extracts filtered prior to TOC analysis? Sonication will quite likely get some insoluble matter off the filter as well. One way to check would be to run OC/EC analysis on the remaining (post-sonication) filter, if it is still intact.

Reply: The water extracts was filtered using PTFE-membrane single-use syringe filters (Sartorius Minisart SRP 15). Unfortunately this was left out from the original manuscript. This part of the sample preparation has now been added to section 2.2.1. (See also comment regarding this made under bulletpoint 3.

9.Section 3.1: Blank OC levels were "$<$0.5 μg/m3 for 13 of the 14 sites" - that seems rather high considering these are background sites. Could these be reduced further?

Reply: Although sampling was performed in background areas, handling, transport, conditioning, storing, and so fort might add to the field blank level as well. Thus, the major contribution to the field blank level might have been obtained at other places than at the background site.

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The filters could not be stored at low temperature, which appears to be standard procedure between ended sampling and subsequent analysis, until the filters were returned to NILU from the various sampling sites across Europe for analysis. Further, the filters were conditioned for 48 hours prior to, and after being exposed, as the mass concentration was to be determined. Typically, one try to avoid obtaining levels of OC and mass concentration from the same filter to keep the field blank level low with respect to OC. Thus, it could be speculated that the field blank levels would have been lower if the filters were to be analyzed with respect to EC and OC only.

10.Page 3865, lines 7-10: The presented concentrations are not field blank-corrected. The reason given is rather strange - "field blank OC level could be reduced by as much as a factor of two when inserted into the sampler and letting particulate free air flow through". Do the authors have any data to back up this statement, or any reference? There appears to be plenty of data to the contrary - e.g. any artifact measurements on backup filters are exposed to particle-free air, yet the OC on the backup filters is much higher than field blank levels. Granted, they sample particle-free air for long periods, but that still satisfies the author's condition and yet disproves their claim.

Reply: See bulletpoint 1.

11.Page 3866, lines 6-8: The authors should also consider the fact that most of the results in the table are at urban sites, whereas the study most comparable to the EMEP program is the Putaud and Cavalli (2006) study at a rural site. Also, the QBT method is usually a better estimator of the positive artifact.

Reply: The referee's comment has been accounted for and the following sentence has been included to account for the fact that the sites in the present study are mainly rural background sites, while those listed in Table 3 are mainly urban sites:

ůSince the majority of the OC concentrations from the EMEP campaign (Table 4) are in the lower range of those listed in Table 3, the positive artefact is likely to be more severe. Indeed, Putaud and Cavalli (2006) reported that the positive artefact was most

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severe for samples with a low OC loading. In addition, the majority of the sites listed in Table 3 are urban sites while those included in the present study are rural background sites.

On page 3865 lines 23-24 we already stated that the majority of the studies performing such corrections are situated in urban areas.

ůThe referee states that the QBT method usually is a better estimator of the positive artefact compared to the QBQ method. We agree that the QBT-approach provides a higher estimate of the positive artefact compared to the QBQ-approach, and we state this on page 3866 lines 3-5. The difference between the two approaches tends to decrease with increased sampling time, however, what is the better or more correct approach still remains a bit unclear.

12.Page 3866, lines 10-17: The seasonal variation in positive artifact is suggested as caused by lower levels of particulate OC in the summer relative to winter. Are the authors considering absolute values of the artifact, or relative to the particulate OC? In any case, the summer levels of OC are higher than the winter concentrations in the study by Subramanian et al. (2004), which contradicts the results of Viana et al. and thus the argument proposed by the authors. In any case, this result is really from the work of others (Viidanoja et al.) and not the present study, and so this paragraph seems out of place, because the authors don't really use the results anyway.

Reply: We were considering the relative contribution.

Our intension with this paragraph was to provide a basis of understanding for how the positive artifact, as measured by QBQ and QBT, might vary according to season. However, based on the referees argument that we don't use this text to explain our results, we will remove it from the manuscript

13.Figure 1: The axis ticks are unreadable. Are they all plotted to the same scales (e.g. 0-10 μg/m3)? Making such same-scale plots or if already implemented, stating

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this fact in the figure caption would improve the readability of the figure.

Reply: To increase the readability of Figure 1, the following sentence has been included in the figure caption.

Fig. 1. Spatial distribution of the sampling sites participating in the campaign and their annual mean concentration of EC, OC and TC (μg\m3) for the period 1 July 2002 - 1 July 2003. The figures are all plotted to the same scales (0-10 μg/m3).

14.Section 3.2: The EC levels in EMEP are much higher (˜3x) than for the IMPROVE sites; also, the IMPROVE protocol usually measures more EC (˜2x) than a NIOSH-type protocol. Put this together, and the EC levels at the EMEP sites are actually much higher (˜6x) than what has been found in rural sites in the US!! Can the authors explain why this is so? (A PM10 vs PM2.5 reason is probably not appropriate since EC is usually found in the fine aerosol.) Also, the Braganza site, which is southern-most of all EMEP sites, actually shows much less EC than at least three northern sites (Ispra, Illmitz, Stara Lesna) - an equally good explanation appears to be a coastal-to-continental transition, with sites closer to waterbodies showing lower EC values than inland sites. Could the authors comment? (A similar comment could be made for OC.)

Reply: Unfortunately we do not know the answer to why the levels are considerably higher at European rural background sites compared to those obtained in the IMPROVE network in the US, hence we can only speculate about the reason:

a)The rural background sites in Europe and the sites in the IMPROVE network in the US are not representative for the same type of environment. The IMPROVE sites are mainly situated in national parks, which potentially might be rather pristine, at least in the Western states and the Rocky Mountain parts of the country, which also have the greatest number of sites. Europe is fairly densely populated and the distance from urban areas to rural background sites might be less in Europe compared to the US.

b)Europe has a large fraction of low duty vehicles besides trucks that run on diesel,

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and this fraction is increasing. In the US, it is mainly the trucks that use diesel.

c)We agree with the referee that the majority of EC resides in the fine fraction, and that the difference in size-fraction between the two studies is not nearly enough to explain the difference observed.

The referee is correct when stating that the level of EC at Braganza is lower than that observed at Illmitz and Ispra. Being situated much closer to the sea than the sites situated in Central Europe, it is likely that Braganza is more influenced by non-polluted marine air masses. When such air masses enters the European continent they are likely to pick up PM pollution, and hence the PM concentration will increase with increasing residence time over land. Hence, it is not unlikely that also this effect contributed to the North to south gradient observed.

15.Comparison of EMEP results with IMPROVE data: Have the authors considered the effect that the size fraction the two studies use could have on the seasonal trends, e.g. biogenic species being more prominent in PM10 than PM2.5?

Reply: The common assumption is that biogenic sources of OC contribute to the fine fraction of PM (i.e. BSOA), although we argue (present study) that for certain parts of Europe (Scandianavia), biogenic sources contributing to the coarse fraction (Primary Biological Aerosol Particles = PBAP) could be equally important. If the US sites experience an increase in coarse biogenic OC, as we claim for Scandinavia, this is also likely to contribute the most during summer. Hence, the seasonal variation for OC in PM10 for non-urban sites in the IMPROVE network would be the same as they report for OC in PM2.5, only more pronounced.

In our study, the increase of OC in PM10 during summer is seen for those sites experiencing the lowest levels of OC, that is those sites likely to be influenced the least by anthropogenic sources. Hence, it is not unlikely that size segregated data for the least anthropogenic influenced sites in the IMPROVE network could show a similar seasonal variation for coarse OC as observed in the present study. Indeed, this would have been

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interesting to study more closely given the large number of sites in the IMPROVE network.

If coarse biogenic OC is present in the urban environment where the 4 urban sites in the IMPROVE network are situated, we could only speculate whether it's source strength would be strong enough to make the seasonal variation of OC in PM10 peak in summer rather than winter as seen for OC in PM2.5.

16.Figure 5: Could you please mark the sites on the plots - it is very hard to tell where the site is located.

Reply: The sites on the plots have been magnified, hence they should now be visible.

17.Coarse contribution to PM10: "PM10 might be subject to positive artifacts, while this is not the case for coarse OC" - add some explanation why (restating that the artifact from PM2.5 and PM10 measurements cancel out is sufficient). This may not be immediately clear.

Reply: The clarification requested by the referee has been included:

"It is likely that the relative contribution is even higher, as OC in PM10 might be subject to positive artefacts, while this is not the case for coarse OC, as the artifact from PM2.5 and PM10 cancel each other".

18.See earlier comment on measurement of WSOC and WINSOC.

Reply: See bullet point 3 regarding the issue on WSOC and WINSOC measurements.

19.What are the blank levels for PM10 mass measurements? Quartz filters are rather brittle, so post-weighing after sampling/transport could affect the observed mass concentrations.

Reply: See bullet point 2 regarding blank levels for PM10 mass measurements.

20.RM8785 is the fine fraction of resuspended urban aerosol, whereas the EMEP re-

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sults are for PM10 from mostly rural sites. The authors have earlier shown that PM10 has a greater biogenic influence at least at one site, compared to PM2.5. How do the authors then justify using the IMPROVE/NIOSH comparison (which likely depends on the sample matrix) from RM8785 for the EMEP samples?

Reply: The statement raised by the referee is sound, and we agree that the best alternative would be to make such a comparison based on a standard reference material that was collected on an European rural site rather than at an US urban site. However, RM8785 is the only reference material for EC/OC available that we are aware of. To optimize such a comparison, samples from each of the 14 sites, collected at various seasons should have been subjected to both the Quartz.par protocol, used in the present study, and the IMPROVE protocol. However this would have required a large additional number of analyses (1 sample pr season pr site, provides 1 x 4 x 14 = 56 samples) by an instrument/protocol that we don't have access to.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 3859, 2007.